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Additivity relations for the heat capacities of nonelectrolytes in
aqueous solution

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Short title: Additivity in aqueous $C_{p,2}^{\infty}$ values of nonelectrolytes

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Abstract

A simple additivity scheme is derived for the partial molar heat capacities of nonionic compounds in infinitely dilute aqueous solution at 298 K. Calculated group parameters are based on several homologous series of compounds of the type $\text{H}-(\text{CH}_2)_n-\text{X}$ and the internal agreement of the system is shown. The effects of branching and cyclization are discussed. Predicted partial molar heat capacity values are compared with experimental results.

1. Introduction

In order to facilitate the interpretation of results from thermodynamic experiments on biochemical systems it is common to rely upon data for simple model compounds in aqueous solutions. This approach has e.g. been used frequently in discussions of the thermodynamics of binding and denaturation processes of biopolymers. It is also largely through studies of very simple solutes that the present ideas regarding 'hydrophobic interactions' in biochemical systems have developed. For reviews pertinent to the field see e.g. references 1-4.

When thermodynamic data for biochemical models are considered, it is usually assumed that simple additivity rules can be applied to the component groups. However, although considerable effort has been directed to additivity relationships for pure substances⁽⁵⁾, very little has been done to check whether it is possible to consider the basic thermodynamic variables as constitutive and additive properties of molecules in the dissolved state, particularly in aqueous solution.

The partial molar heat capacity at infinite dilution, $C_{p,2}^{\infty}$, is one of the more interesting variables to correlate since it seems to reflect interactions between hydrophobic groups and bulk water.⁽¹⁾ For instance, low molecular weight hydrocarbons have aqueous $C_{p,2}^{\infty}$ values which are about three times larger than the heat capacities for the pure liquid compounds.^(6,7)

The discussions in this paper are based primarily on the results from a series of calorimetric investigations earlier reported from this laboratory,^(6, 8-12) but results from other recent calorimetric studies have also been included. All $C_{p,2}^{\infty}$ values used refer to 298 K.

In the earlier reports it was shown that for several homologous series $C_{p,2}^{\infty}$ values increase linearly with the number of carbon groups, n :

$$C_{p,2}^{\infty} = a + b \cdot n \quad (1)$$

The CH_2 increment, b , was, in most cases, found to be around $90 \text{ J K}^{-1} \text{ mol}^{-1}$. For the alcohol and carboxylic acids series,⁽⁸⁾ and more recently for amides,⁽¹²⁾ it was noted that $C_{p,2}^\infty$ values for the parent compounds ($n=0$, i.e. H_2O , HCOOH and HCONH_2 , respectively) were rather close to the intercept value, a , as predicted by eqn (1). The effect of branching of the alkyl chain was found to be small or insignificant.

It is the purpose of this paper to investigate more generally how accurately the observed additivity relationships hold for aqueous $C_{p,2}^\infty$ values of nonionic compounds. It will be assumed that $C_{p,2}^\infty$ values can be expressed as the sum of a number of parameter values, $\phi(Y)$, each referring to the constituent atoms or groups of atoms, Y , of the molecule.

2. Development of additivity parameters

VALUE FOR THE CH_2 GROUP

Table 1 summarizes CH_2 -increments, $\phi(\text{CH}_2)$, for several series of linear monofunctional aliphatic compounds, $\text{H}-(\text{CH}_2)_n\text{-X}$ (the individual $C_{p,2}^\infty$ values are listed in table 7). For each series mean values are given and mean values have also been derived for the increment of each step. Data for alkyl substituted benzenes ($n=0-3$) have also been determined,⁽¹⁰⁾ but the values for $n=2,3$ are rather uncertain and the series has therefore not been included in table 1.

Inspection of the table shows that the value for the step $n=6$ to $n=7$ in the alcohol series and the first value in the carboxylic acid series are outside the general pattern. Values for hexanol and heptanol are both uncertain ($\pm 23 \text{ J K}^{-1} \text{ mol}^{-1}$), whereas the values for formic acid and acetic acid are believed to be accurate. If the divergent values are excluded the mean value for the different series, as well as for the different steps,

is found to be close to $90 \text{ J K}^{-1} \text{ mol}^{-1}$. The overall mean value is identical $(89.5 \pm 0.7) \text{ J K}^{-1} \text{ mol}^{-1}$ being to the mean value obtained by a least squares fit, $(89.6 \pm 0.7) \text{ J K}^{-1} \text{ mol}^{-1}$.

The values given in table 1 show that the CH_2 -increment for compounds of the type $\text{H}-(\text{CH}_2)_n\text{-X}$ is essentially constant and it is thus concluded that the nature of the X group normally does not markedly affect the $\phi(\text{CH}_2)$ value.

VALUES FOR THE PARENT COMPOUNDS

It is interesting to note that even for the step $n=0$ to $n=1$ (carboxylic acid series not included) the CH_2 -increment is very close to the overall mean value. Parameter values for hydrogen and for the functional groups (X) thus appear to be the same whether they are covalently linked to each other or if they are separated by one or more methylene groups.

This condition can be expressed as

$$C_{p,2}^{\infty}(\text{H-X}) = \phi(\text{H}) + \phi(\text{X}) \quad (2)$$

and (cf. eqn 1)

$$C_{p,2}^{\infty}(\text{H-X}) = C_{p,2}^{\infty}(\text{H}-(\text{CH}_2)_n\text{-X}) - n\phi(\text{CH}_2) \quad (3)$$

With these prerequisites $C_{p,2}^{\infty}$ values for the parent compounds ($n=0$) were derived using equation (1). The value for $b (= \phi(\text{CH}_2))$ was taken to be $90 \text{ J K}^{-1} \text{ mol}^{-1}$ and the intercept values were obtained by a least squares treatment of experimental $C_{p,2}^{\infty}$ values for $n \geq 0$. (Values for formic acid, benzene and heptanol were not included.) Calculated and experimental $C_{p,2}^{\infty}$ values for the parent compounds are shown in table 2. Where more than one experimental value is available, mean values were used. It is seen that the calculated value for benzene is significantly lower than the experimental value.

The good agreement between calculated and experimental values for most of the parent compounds support the assumption made that the $C_{p,2}^{\infty}$ parameter values for H, CH_2 and X are additive and that the individual $\phi(Y)$ values can be derived as shown below.

PARAMETER VALUES FOR HYDROGEN AND FOR THE DIFFERENT POLAR GROUPS

As with equations (2) and (3), a system of three equations can be written for the parent compounds H_2O , $\text{HOCH}_2\text{CH}_2\text{OH}$ and $\text{HOCH}_2\text{CH}_2\text{OCH}_3$:

$$C_{p,2}^{\infty}(\text{H-OH}) = \phi(\text{H}) + \phi(\text{OH}) \quad (4)$$

$$C_{p,2}^{\infty}(\text{H-O-CH}_2\text{CH}_2\text{-OH}) = \phi(\text{H}) + \phi(\text{OH}) + \phi(\text{O}) + 2\phi(\text{CH}_2) \quad (5)$$

$$C_{p,2}^{\infty}(\text{H-O-CH}_2\text{CH}_2\text{-O-CH}_2\text{-H}) = 2\phi(\text{H}) + 2\phi(\text{O}) + 3\phi(\text{CH}_2) \quad (6)$$

It was thus assumed that the CH_2 -groups in $\text{R-OCH}_2\text{CH}_2\text{OH}$ and $\text{R-OCH}_2\text{CH}_2\text{OMe}$ all have the normal value of $90 \text{ J K}^{-1} \text{ mol}^{-1}$. Parameter values for H, OH and O were calculated by solving the above system of equations using the calculated $C_{p,2}^{\infty}$ values for the parent compounds. Results are summarized in the first row of table 3.

By another approach values for $\phi(\text{OH})$, $\phi(\text{NH}_2)$ and $\phi(\text{COOH})$ can be derived from $C_{p,2}^{\infty}$ values for α,ω -difunctional compounds, $\text{X-(CH}_2)_n\text{X}$. However, it was shown⁽¹¹⁾ that for the lower members of these series there is a systematic deviation from the linear relationship of equation (1). For the diols a constant $\phi(\text{CH}_2)$ value was found for $n > 3$ ($n = 4, 5, 6$) whereas the constant, close to normal increment value appeared to be reached for $n = 4$ and $n = 5$ for the diamines and the dicarboxylic acids, respectively.

The normal $\phi(\text{CH}_2)$ value ($90 \text{ J K}^{-1} \text{ mol}^{-1}$) and the experimental $C_{p,2}^{\infty}$ values for $n = 4, 5$ and 6 of the diol series and for $\text{H}_2\text{N-(CH}_2)_4\text{-NH}_2$ and $\text{HOOC-(CH}_2)_5\text{-COOH}$ were used to obtain $\phi(X)$ values according to equation 7.

$$2\phi(X) = C_{p,2}^{\infty}(X-(CH_2)_n-X) + n\phi(CH_2) \quad (7)$$

The derived $\phi(X)$ values were combined with the corresponding calculated values for H-X (Table 2) and $\phi(H)$ values were then calculated by applying equation (2). $\phi(Y)$ values calculated by this approach are also summarized in table 3.

The $\phi(H)$ values derived from data for the α,ω -compounds are somewhat higher than those based on $C_{p,2}^{\infty}$ data for alcohols and the glycol derivatives. It should be noted, however, that the normal or close to normal CH_2 -increments found for the higher α,ω -compounds do not imply that these compounds actually are "normal" using the monofunctional compounds as a reference (cf. Schrier et al.⁽¹³⁾). We therefore favour the set of parameters listed in the first row of table 3 which will be used as the starting point of subsequent additivity operations discussed in this paper.

$\phi(X)$ values were obtained by subtracting the $\phi(H)$ value ($67 \text{ J K}^{-1} \text{ mol}^{-1}$) from the calculated values for the parent compounds, table 2. Corresponding ϕ values for CH_3- , $-CH-$ and $-\overset{|}{C}-$ were obtained from the value for $\phi(CH_2)$. Derived parameter values are summarized in table 4. All $\phi(Y)$ values refer to 298 K. However, our experimental work has indicated that $C_{p,2}^{\infty}$ values have a very low temperature coefficient. Derived parameter values are therefore judged to be relevant at least for the temperature region 290-310 K.

3. Branching and cyclization effects

BRANCHING OF ALKYL CHAINS

The effect of branching of alkyl chains can be evaluated by comparing available data for the pairs of compounds PrX, i-PrX; BuX, i-BuX and

BuX, t-BuX. It must then be assumed that, as for straight chain compounds, there is no influence from the polar groups on the value for the branched alkyl chains. Data for such pairs of compounds are shown in table 5, where the straight chain compounds are represented by values obtained using the additivity parameters derived in the preceding section. It is seen that differences between Pr and i-Pr compounds, including BuX, i-BuX, are insignificant. For the BuX, t-BuX pairs, however, there appears to be a varying but significant decrease in $C_{p,2}^{\infty}$ accompanying a branching process, except for the alcohol pair, where the well established experimental values indicate a significant effect in the opposite direction. A comparison between heat capacity values for the pure straight chain and branched alkyl compounds in the gas phase shows only marginal differences and the same applies to heat capacities for pure liquid hydrocarbons.⁽⁷⁾

Until more data are available we tentatively assume that branching from n- to i- produces no change in $C_{p,2}^{\infty}$ whereas branching n- to t- seems to produce a decrease in $C_{p,2}^{\infty}$ amounting to about $-30 \text{ J K}^{-1} \text{ mol}^{-1}$. The conflicting alcohol data, however, suggests that this assessment should be used with care.

THE CYCLIZATION EFFECTS

In all cases where a comparison can be made of a straight chain compound and the corresponding cyclic compound, the $C_{p,2}^{\infty}$ values for the former are substantially higher. Table 6 shows the differences in $C_{p,2}^{\infty}$ for several such pairs.

Branching of alkyl chains were shown to lead to no or moderate changes in aqueous $C_{p,2}^{\infty}$ values. This suggests that the large decrease in $C_{p,2}^{\infty}$ following cyclization processes is not primarily due to decreased exposure of the hydrocarbon surface to water as has been suggested.⁽¹⁴⁾

It rather appears to be mainly associated with the loss of the two hydrogens,

which alone will account for an effect of about $-130 \text{ J K}^{-1} \text{ mol}^{-1}$. In addition one may expect a decrease in $C_{p,2}^{\infty}$ due to loss of internal degrees of freedom associated with the cyclizing. A comparison of CH_2 -increments for pure straight chain and cyclic liquid alkanes (C_4 - C_8) gives a mean decrease on cyclization of about $20 \text{ J K}^{-1} \text{ mol}^{-1}$.⁽⁷⁾ One might, therefore, expect a total decrease in the aqueous $C_{p,2}^{\infty}$ values upon cyclization of approximately $155 \text{ J K}^{-1} \text{ mol}^{-1}$. In most cases this value is judged to be within limits of the experimentally observed values, table 6. It appears, however, as if specific effects between the different solutes and the water are also significant.

4. Application of group parameters

CONFIRMATION OF INTERNAL AGREEMENT

Since the group parameters have been derived from the n-alkyl homologs of the various series of compounds, it is of interest to show that the parameters accurately predict $C_{p,2}^{\infty}$ values of these compounds. Table 7 lists experimental and predicted values for six different series of straight chain compounds (the two amide series have been combined) and the differences between these values. It is seen that in most cases the differences are of the same order as the uncertainties assigned to the experimental values.

The derived set of parameter values were based on $C_{p,2}^{\infty}$ values from a limited number of key compounds. Other values might have been chosen; e.g. the mean of the $\phi(\text{H})$ values listed in table 3. It should be noted, however, that essentially the same agreement would have been obtained between experimental and calculated values for compounds of the type $\text{H}-(\text{CH}_2)_n-\text{X}$.

For the alcohol series it may be noted that the experimental values for hexanol and for heptanol are uncertain. (The value for heptanol was

not used in the development of the additivity parameters.) The present comparison suggests that the experimental $C_{p,2}^{\infty}$ value for hexanol is correct but that the calculated value for heptanol, $706 \text{ J K}^{-1} \text{ mol}^{-1}$, is more reliable than the experimental value, $(737 \pm 23) \text{ J K}^{-1} \text{ mol}^{-1}$.

The values for diethoxyethane and formamide were not used in the development of the additivity parameters as they do not belong to any of the series utilized. It is seen, however, that the experimental values of these compounds agree well with the calculated values.

AQUEOUS $C_{p,2}^{\infty}$ VALUES FOR HYDROCARBONS

Experimental $C_{p,2}^{\infty}$ data for hydrocarbons in aqueous solution have been difficult to determine because of their low solubilities. The agreement between values derived by different workers has often been poor which to a large extent seems to be due to the differences in methods used for evaluation of the experimental results, cf. reference 9. Recently,⁽⁶⁾ calorimetric determinations have been made in this laboratory for pentane, hexane, cyclohexane as well as for several aromatic hydrocarbons. In table 8 experimental $C_{p,2}^{\infty}$ values for some hydrocarbons in aqueous solution are compared with corresponding values calculated from the group values given in table 3.

It is seen that for the lower aliphatic hydrocarbons the agreement between calculated values and values derived from solubility data are very divergent. The values derived by Alexander et al.⁽²³⁾ for methane and ethane agree fairly well with the calculated value whereas for propane the agreement is better with the value reported by Wauchope and Haque.⁽²⁴⁾ For butane both values derived from experimental data are much lower than the predicted value. The agreement between the calorimetric and predicted values for pentane and hexane is within expected uncertainty limits. The calculated values are shown to be consistent with the calorimetric data and

it is therefore judged that the predicted values are generally more reliable than those derived from solubility data. In particular we believe this is true for the butane value.

For cyclohexane calculated and predicted values agree within expected uncertainty limits, cf. table 6.

The agreement between experimental and calculated values is satisfactory for toluene, ethylbenzene and propylbenzene. However, as noted earlier, the value calculated for the parent compound, benzene, is significantly lower than the well documented experimental value.

APPLICATION OF THE ADDITIVITY SCHEME TO OTHER TYPES OF COMPOUNDS

In tables 9-12 are shown the results from application of the group parameters to several series of compounds.

For the α,ω -difunctional compounds, table 9, the calculated values are generally lower than the experimental results. It was noted earlier⁽¹¹⁾ that the CH_2 increments for these compounds are low, but increasing with n . It was suggested that the effect could be due to temperature dependent equilibria e.g. the breaking of hydrogen bonds.

The aromatic compounds listed in table 10, except for the alkyl-phenols, can also be looked upon as α,ω -disubstituted alkyl compounds. The two series measured are short but the precision of the values is good enough to indicate that the CH_2 -increments are significantly lower ($\sim 70 \text{ J K}^{-1} \text{ mol}^{-1}$) than in the normal value. The experimental value for phenoxyethanol is substantially larger than the calculated value.

Several secondary and tertiary amines are listed in table 11. The calculated values were obtained by assuming that $\phi(\text{NH}) = \phi(\text{NH}_2) - \phi(\text{H})$ and $\phi(\text{N}) = \phi(\text{NH}_2) - 2\phi(\text{H})$. As seen in the table this procedure gives acceptable agreement between experimental and predicted values for some of the compounds

but that in most cases the calculated values are substantially lower than the experimental results.

The exceptionally large difference between the experimental $C_{p,2}^{\infty}$ values for Me_2NH and EtNHMe , $156 \text{ J K}^{-1} \text{ mol}^{-1}$, is surprising. Corresponding differences between Et_2NH , PrNH_2 and Pr_2NH are normal, ca. $85 \text{ J K}^{-1} \text{ mol}^{-1}$.

For the hydroxyl compounds listed in table 12 the agreement between experimental and calculated values are in most cases good. Notable exceptions are sucrose and tris(hydroxymethyl)aminomethane.

The calculated value for urea is also very different from the experimental value.

5. Conclusions

The additivity correlations summarized here may be used for empirical estimates of aqueous $C_{p,2}^{\infty}$ values at 298 K, in particular for monosubstituted alkyl compounds, RX . Accurate aqueous $C_{p,2}^{\infty}$ values are sometimes difficult to determine, e.g. for slightly soluble compounds. In such cases the present additivity scheme appears to lead to more reliable values than those derived from moderately accurate calorimetric work or from even very careful solubility studies (cf. e.g. the conflicting results of measurements on hydrocarbons). It may be noted that the scheme has not yet been tested on compounds for which R is an alkyl chain with $n > 8$. One may expect that for very long chains there will be a tendency for intramolecular hydrophobic interactions which would be expected to reduce the $C_{p,2}^{\infty}$ values.

Another as important use of a consistent set of additivity parameters is to indicate compounds which have "abnormal" $C_{p,2}^{\infty}$ values and which thus may be worth a close study. It should then be noted that the "abnormal" compounds may not be abnormal per se but are those which

deviate visavi the simple alkyl compounds used for development of the additivity parameters. Such deviations may indicate specific solute-water interactions (or the lack of such interactions) or they may be the sign of intramolecular interactions such as temperature dependent hydrogen bond equilibria. Prominent examples of such "abnormal" values are those which we found for sucrose and tris(hydroxymethyl)aminomethane (table 12) which deviate markedly from the other hydroxy compounds investigated.

It should be kept in mind that the present additivity correlations are the result of a formal treatment and that it may not be permissible to use them for an interpretation of the nature of the "hydrophobic effects" being reflected in the exceptionally large $C_{p,2}^{\infty}$ values. However, it is an interesting observation that $\phi(H)$ is large and positive whereas (ether) oxygen and polar groups containing oxygen and nitrogen are near zero or negative. In fact, the present additivity scheme suggests that it is the hydrogen atoms which are responsible for the exceptionally large $C_{p,2}^{\infty}$ values for hydrophobic compounds (consisting of C, H, O and N atoms) in aqueous solution. We further find it rather remarkable that a constant value is found for hydrogen regardless if it is bound to carbon, nitrogen or to oxygen. The "hydrogen effect" will be more generally discussed elsewhere.⁽³¹⁾

The $C_{p,2}^{\infty}$ values for homologous series give in most cases a straight line relationship (eqn. 1), even when $n=0$ is included. Together with the normally small effect of branching of the alkyl chains, this fact seems to support the view (reference 1, p. 7) that the solute-water interactions as reflected by excess heat capacity values have the nature of short range effects.

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TABLE 1. CH_2 -increments ($\delta(\text{CH}_2)$; $\text{J K}^{-1} \text{ mol}^{-1}$) in the aqueous $\text{C}_{\text{p},2}^\infty$ values for some monofunctional compounds,
 $\text{H}-(\text{CH}_2)_n-\text{X}$.

Homologous series	Step							Mean CH_2 - increment	Least squares CH_2 -increment
	0→1	1→2	2→3	3→4	4→5	5→6	6→7		
$\text{H}-(\text{CH}_2)_n-\text{OH}$	83	99	98	83	89	84	(126)	89.3	90.2
$\text{H}-(\text{CH}_2)_n-\text{NH}_2$	80	86 ^a	86 ^a	95	93	89		88.2	88.7
$\text{H}-(\text{CH}_2)_n-\text{COOH}$	(70)	88	84	95				89.0 ^b	88.5 ^b
$\text{H}-(\text{CH}_2)_n-\text{CONHMe}$	94	76	100	90				90.0	89.6
$\text{H}-(\text{CH}_2)_n-\text{NHCOMe}$	98	85	94	79				89.0	89.1
$\text{H}-(\text{CH}_2)_n-\text{OCH}_2\text{CH}_2\text{OH}$	97	97	81	88				90.8	90.4
$\text{H}-(\text{CH}_2)_n-\text{OCH}_2\text{CH}_2\text{OMe}$	90	83	100	89				90.5	90.7
Mean CH_2 -increment	90.3	87.7	91.9	88.4	91.0	86.5		89.5 ± 0.7	89.6 ± 0.7

^aMean increment between MeNH_2 and PrNH_2

^bFor $n \geq 1$

TABLE 2. Calculated and experimental $C_{p,2}^{\infty}$ values for parent compounds, H-X.

Compound	$C_{p,2}^{\infty}/J\ K^{-1}\ mol^{-1}$	
	calculated	experimental
H-OH	76	75.3
H-NH ₂	65	75 ^a
H-COOH	72	95.5 ± 1.0 ^b
H-CONHMe	163	164 ± 2 ^c
H-NHCOMe	163	160 ± 1 ^c , 163.8 ± 1 ^d
H-OCH ₂ CH ₂ OH	199	193 ± 2 ^e , 191.9 ± 0.1 ^f
H-OCH ₂ CH ₂ OMe	290	290 ± 4 ^g
H-C ₆ H ₅	333	361 ± 5 ^h , 374 ± 2 ⁱ

^aReference 14. ^bReference 8. ^cReference 12. ^dReference 15.

^eReference 11. ^fReference 16. ^gReference 9. ^hReference 6. ⁱReference 17.

TABLE 3. Derivation of group parameter values, $\phi(Y)/J\ K^{-1}\ mol^{-1}$

Key compounds	$\phi(H)$	$\phi(OH)$	$\phi(O)$	$\phi(NH_2)$	$\phi(COOH)$
$R-OH, R-OCH_2CH_2OH, R-OCH_2CH_2OMe$	67	9	-57		
$R-OH, HO-(CH_2)_n-OH; n=3,4,5$	82	-6			
$R-NH_2, H_2N-(CH_2)_4-NH_2$	75			-10	
$R-COOH, HOOC-(CH_2)_5-COOH$	92				-20

TABLE 4. Group parameter values, $\phi(Y)/J\ K^{-1}\ mol^{-1}$

Functional group	Parameter value	Functional group	Parameter value
CH ₃	157	O (ether)	-57
CH ₂	90	NH ₂	-2
CH	23	NHCO	-61
C	-44	COOH	5
H	67	C ₆ H ₅	266
OH	9		

TABLE 5. Effect of branching of alkyl chain

	$C_{p,2}^{\infty}/J\ K^{-1}\ mol^{-1}$		
	Experimental	Calculated	Difference
i-PrOH	359 ± 16^a	346	13
i-BuOH	432.5 ± 0.4^b	436	-4
i-PrNH ₂	342 ± 18^c	335	7
i-BuNH ₂	416 ± 9^c	425	-9
i-PrCOOH	334 ± 2^c	342	-8
i-PrCONHMe	431 ± 6^c	433	-2
i-PrNHCOMe	441 ± 5^c	433	8
t-BuOH	$463 \pm 6^d, 464.0 \pm 0.6^b$	436	27, 28
t-BuNH ₂	403 ± 7^c	425	-22
t-BuCOOH	417 ± 9^c	432	-15
t-BuCONHMe	476 ± 7^c	523	-47
t-BuNHCOMe	498 ± 5^c	523	-25

^aReference 18. ^bReference 16. ^cReference 8. ^dReference 12.

TABLE 6. The heat capacity effect of cyclization, $\Delta C_{p,2}^{\infty}/J\ K^{-1}\ mol^{-1}$.

Process	$\Delta C_{p,2}^{\infty}$
Et ₂ NH → pyrrolidine	
487 ^a 333 ^a	-154
Et ₂ NMe → N-methylpyrrolidine	
533 ^a 450 ^a	-83
PrNHEt → piperidine	
570 ^a 425 ^a , 405.0 ^b	-145, -165
n-HexNH ₂ → c-hexylamine	
605 ^c 481 ^d	-124
MeOCH ₂ CH ₂ OH → 1,3-dioxolan	
289 ^c 175 ^a	-114
n-hexane → c-hexane	
674 ^c 516 ^e	-158
MeOCH ₂ CH ₂ OMe → 1,4-dioxane	
380 ^c 212 ^a , 222.4 ^b , 195 ^f	-168, -158, -185
BuOH → tetrahydrofuran	
436 ^c 295 ^a	-141
PeOH → 2-methyltetrahydrofuran	
526 ^c 435 ^a	-91
PeOH → tetrahydropyran	
526 ^c 373 ^a , 384.9 ^b	-153, -141
Me ₂ NH → 1/2 piperazine	
263 ^a 132 ^b	-131 ^g

^aReference 14. ^bReference 19. ^cCalculated value (cf. table 7). ^dReference 20.

^eReference 6. ^f $\Delta C_{p,soln}^{\infty}$ from reference 21 and C_p^x from reference 7. ^gThis process is not strictly comparable to one where a single open chain molecule will form a cyclic structure.

TABLE 7. Experimental and calculated aqueous $C_{p,2}^{\infty}$ values at 298.15 K for the series of compounds used in derivation of group parameter values.

	$C_{p,2}^{\infty}/J\ K^{-1}\ mol^{-1}$		
	Experimental	Calculated	Difference
Alcohols:			
MeOH	$157 \pm 8^a, 158.2 \pm 0.1^b$	166	-9, -8
EtOH	$253 \pm 11^a, 260.3 \pm 0.1^b$	256	-3, 4
PrOH	$358 \pm 17^a, 352.9 \pm 0.2^b$	346	12, 7
BuOH	$439 \pm 21^a, 437.0 \pm 0.5^b$	436	3, 1
PeOH	$530 \pm 7^c, 523.8 \pm 0.3^b$	526	4, -2
HexOH	611 ± 23^d	616	-5
HepOH	737 ± 23^d	706	31
Amines:			
MeNH ₂	155^e	155	0
EtNH ₂	-	245	-
PrNH ₂	327 ± 5^f	335	-8
BuNH ₂	422 ± 4^f	425	-3
PeNH ₂	515 ± 5^f	515	0
HexNH ₂	$605 \pm 4^g, 603 \pm 6^f$	605	0, -2
Carboxylic acids:			
HCOOH	95.5 ± 1.0^f	72	24
MeCOOH	165 ± 3^f	162	3
EtCOOH	253 ± 3^f	252	1
PrCOOH	337 ± 3^f	342	-5
BuCOOH	432 ± 7^f	432	0

Cont.

TABLE 7, cont.

	$C_{p,2}^{\infty}/J\ K^{-1}\ mol^{-1}$		
	Experimental	Calculated	Difference
Alkoxyethanols:			
$MeOCH_2CH_2OH$	290 ± 4^h	289	1
$EtOCH_2CH_2OH$	387 ± 5^h	379	8
$PrOCH_2CH_2OH$	468 ± 5^h	469	-1
$BuOCH_2CH_2OH$	556 ± 7^h	559	-3
Dialkoxy-ethanes:			
$MeOCH_2CH_2OMe$	380 ± 7^h	380	0
$EtOCH_2CH_2OMe$	463 ± 7^h	470	-7
$PrOCH_2CH_2OMe$	563 ± 7^h	560	3
$BuOCH_2CH_2OMe$	652 ± 10^h	650	2
$EtOCH_2CH_2OEt$	569 ± 7^h	560	9
Amides:			
$HCONH_2$	82 ± 1^c	73	9
$HCONHMe$	164 ± 2^c	163	1
$MeCONH_2$	$160 \pm 1^c, 163.8 \pm 1^i$	163	-3, 1
$MeCONHMe$	258 ± 3^c	253	5
$MeCONHEt$	343 ± 5^f	343	0
$MeCONHPr$	437 ± 5^f	433	4
$MeCONHBu$	516 ± 1^c	523	-7
$EtCONHMe$	334 ± 4^f	343	-9
$PrCONHMe$	434 ± 5^f	433	1
$BuCONHMe$	524 ± 4^c	523	1

^aReference 18. ^bReference 16. ^cReference 12. ^dReference 22. ^eReference 14.

^fReference 8. ^gReference 20. ^hReference 9. ⁱReference 15.

TABLE 8. Experimental and calculated $C_{p,2}^{\infty}$ values for hydrocarbons in aqueous solution at 298.15 K

	$C_{p,2}^{\infty} / \text{J K}^{-1} \text{mol}^{-1}$		
	Experimental	Calculated	Difference
methane	262 ^a , 308 ^b	224	38, 84
ethane	304 ^a , 342 ^b	314	-10, 28
propane	366 ^a , 408 ^b	404	-38, 4
butane	399 ^a , 387 ^b	494	-95, -107
pentane	572 ± 70 ^c	584	-12
hexane	635 ± 45 ^c	674	-39
benzene	361 ± 5 ^c , 374 ± 2 ^d	333	28, 41
toluene	430 ± 13 ^c	423	7
ethylbenzene	504 ± 13 ^c	513	-9
propylbenzene	606 ± 25 ^c	603	3

^aReference 23. ^bReference 24. ^cReference 6. ^dReference 17.

TABLE 9. Experimental and calculated $C_{p,2}^{\infty}$ values for some α,ω -compounds in aqueous solution at 298.15 K.

	$C_{p,2}^{\infty}/J\ K^{-1}\ mol^{-1}$		
	Experimental	Calculated	Difference
$HO-(CH_2)_2-OH$	$193 \pm 2^a, 191.9 \pm 0.1^b$	198	-5, -6
$HO-(CH_2)_3-OH$	269 ± 4^a	288	-19
$HO-(CH_2)_4-OH$	$354 \pm 3^a, 346.8 \pm 0.3^b$	378	-24, -31
$HO-(CH_2)_5-OH$	439 ± 6^a	468	-29
$HO-(CH_2)_6-OH$	$528 \pm 8^a, 521.6 \pm 0.2^b$	558	-30, -36
$H_2N-(CH_2)_2-NH_2$	185 ± 2^a	176	9
$H_2N-(CH_2)_3-NH_2$	256 ± 3^a	266	-10
$H_2N-(CH_2)_4-NH_2$	340 ± 4^a	356	-16
$HOOC-(CH_2)_2-COOH$	225 ± 4^a	190	35
$HOOC-(CH_2)_3-COOH$	271 ± 4^a	280	-9
$HOOC-(CH_2)_4-COOH$	336 ± 10^a	370	-34
$HOOC-(CH_2)_5-COOH$	410 ± 5^a	460	-50

^aReference 11.

^bReference 16.

TABLE 10. Experimental^a and calculated aqueous $C_{p,2}^{\infty}$ values for some aromatic compounds at 298.15 K.

	$C_{p,2}^{\infty}/J\ K^{-1}\ mol^{-1}$		
	Experimental	Calculated	Difference
$C_6H_5-NH_2$	307 ± 2	264	43
$C_6H_5-CH_2-NH_2$	375 ± 2	354	21
$C_6H_5-(CH_2)_2-NH_2$	445 ± 2	444	1
$C_6H_5-(CH_2)_3-NH_2$	516 ± 5	534	-18
C_6H_5-OH	310 ± 2	275	35
$C_6H_5-CH_2-OH$	396 ± 2	365	31
$C_6H_5-(CH_2)_2-OH$	462 ± 3	455	7
$C_6H_5-(CH_2)_3-OH$	530 ± 4	545	-15
$p-HO-C_6H_4-CH_3$	384 ± 2	365	19
$p-HO-C_6H_4-CH_2CH_3$	465 ± 10	455	10
$C_6H_5-OCH_2CH_2OH$	459 ± 2	398	61

^aFrom reference 10.

TABLE 11. Experimental and calculated aqueous $C_{p,2}^{\infty}$ values for some secondary and tertiary amines at 298.15 K ($\phi(\text{NH}) = -69 \text{ J K}^{-1} \text{ mol}^{-1}$; $\phi(\text{N}) = -136 \text{ J K}^{-1} \text{ mol}^{-1}$)

	$C_{p,2}^{\infty} / \text{J K}^{-1} \text{ mol}^{-1}$		
	Experimental	Calculated	Difference
Me_2NH	259 ^a , 263 ^a	245	14, 18
EtNHMe	331 ^a	335	-4
Et_2NH	487 ^a	425	62
PrNHEt	570 ^a	515	55
Pr_2NH	659 ± 17^a , 652 ± 6^b	605	54, 47
Me_3N	397 ^a	335	62
Et_2NMe	533 ^a	515	18
Et_3N	609 ± 5^b	605	4

^aReference 14. ^bReference 20.

TABLE 12. Experimental and calculated aqueous $C_{p,2}^{\infty}$ values for some hydroxy compounds and urea at 298.15 K.

	$C_{p,2}^{\infty}/J\ K^{-1}\ mol^{-1}$		Difference
	Experimental	Calculated ^a	
dimethyl-2,3-propane-diol	432.3 ± 0.3^b	438	-6
1,1,1-tris(hydroxymethyl)ethane	373.3 ± 0.2^b	380	-7
pentaerythritol	328.8 ± 0.2^b	322	7
neo-pentanol	503.5 ± 0.7^b	496	8
glycerol	$279^c, 226^c$	230	49, -4
sucrose	$634^d, 633^e$	281	353, 352
tris(hydroxymethyl)aminomethane	405^f	221	184
urea	87.5 ± 1^g	4	84

^a assuming a t-branching effect of $-30\ J\ K^{-1}\ mol^{-1}$

^b reference 16

^c from heat capacity for the pure compound in reference 25 and two different $\Delta C_{p,soln}^{\infty}$ values in reference 2, p. 351.

^d reference 26

^e reference 27

^f heat capacity for the pure compound from reference 28, $\Delta C_{p,soln}$ from reference 29 and ΔC_p for the protonization reaction in reference 30.

^g reference 15.

